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(71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).			
(72) Inventors: BARBEE, Robert, Boyd; 500 Rambling Road, Kingsport, TN 37663 (US). MATAYABAS, James, Christopher, Jr.; 3429 Wesley Road, Kingsport, TN 37664 (US). TREXLER, Jack, Wesley, Jr.; 1004 South Page Place, Kingsport, TN 37660 (US). PINER, Rodney, Layne; 1301 Jackson Hollow Road, Kingsport, TN 37663 (US).			
(74) Agent: HARDING, Karen, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).			
(54) Title: POLYESTER NANOCOMPOSITES FOR HIGH BARRIER APPLICATIONS			
(57) Abstract			
<p>The present invention relates to a composition comprising a polymer having dispersed therein at least one layered clay material which has been cation exchanged with an organic cation salts represented by Formula (I) wherein M represents either nitrogen or phosphorous; X⁻ represents an anion selected from the group consisting of halogen, hydroxide, or acetate anions, preferably chloride and bromide; R₁ is selected from the group consisting of straight and branched alkyl groups having at least 8 carbon atoms; R₂, R₃, and R₄ are independently selected from straight or branched alkyl groups having 1 to four carbon atoms; and at least one expanding agent which is compatible with said polymer. Preferred polymers include polyesters. The compositions of the present invention show vastly improved platelet separation as evidenced by higher than previously reported basal spacing.</p>			
$\left[\begin{array}{c} R_1 \\ \\ R_2 - M - R_3 \\ \\ R_4 \end{array} \right]^+ X^- \quad (I)$			

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5 **POLYESTER NANOCOMPOSITES FOR HIGH BARRIER**
 APPLICATIONS

Background of the Invention

10 Polyesters such as poly(ethylene terephthalate) (PET) are widely used in
bottles and containers which are used for carbonated beverages, fruit juices, and
certain foods. Because of the limited barrier properties with regard to oxygen,
carbon dioxide and the like, PET containers are not generally used for products
15 requiring long shelf life. It would therefore be desirable to provide improved
barrier properties.

 This invention relates to polyester composite materials having improved
barrier. The polyester composite materials of this invention are useful for forming
packages that have improved gas barrier properties. Containers made from these
polyester composite materials are ideally suited for protecting consumable
20 products, such as foodstuffs, soft drinks, and medicines.

Prior Art

 A. Usuki, M. Kato, A. Okada, T. Kurauchi, J. Appl. Polym. Sci. 63,
137(1997) describes a polypropylene composite that is made by melt mixing
25 polypropylene with an organoclay that has been expanded with a polyolefin
oligomer.

 Y. Kurokawa, H. Yasuda, A. Oya, J. Mater. Sci. Letters. 15,
1481 (1996) describes a polypropylene composite that is made by copolymerizing
diacetone acrylamide and maleic acid modified-polypropylene in the presence of an
30 organoclay and melt mixing with polypropylene.

 T. J. Pinnavaia and Tie Lan, Chem. Mater. 6, 2216 (1994) describes
organoclays that have been expanded with epoxy resin monomers.

 M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, and A. Okada,
Macromolecules, 30, 6333 (1997) describes a polypropylene composite that is
35 made by simple melt-mixing of polypropylene, maleic anhydride modified
polypropylene oligomers, and clays intercalated with stearylammonium ion.

5 U. S. Patent 4,739,007 discloses polyamide composite materials containing layered clay mineral intercalated with organic onium salts.

U. S. Patent 5,164,460 discloses polyimide composite materials containing layered clay mineral intercalated with organic onium salts.

10 WO 93/04118 relates to a process for forming polymeric composites which are comprised of platelet particles containing organic onium salts and dispersed in a polymeric matrix.

U. S. Patent 5,336,647 and 5,429,999 describe the preparation of layered clays containing polyalkoxylated ammonium salts. Use of these clays in polyesters
15 was not recognized.

Among the numerous patents that describe the preparation of layered clays containing ammonium salts are U. S. Pat. Nos. 2,531,427; 2,966,506; 4,081,496; 4,105,578; 4,116,866; 4,208,218; 4,391,637; 4,410,364; 4,412,018; 4,434,075; 4,434,076; 4,450,095; 4,517,112; 4,677,158; 4,769,078; 5,110,501; and 5,334,241.

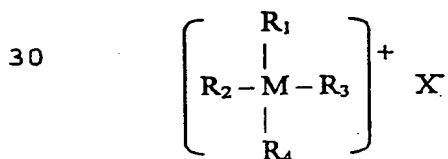
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Description of the Invention

This invention relates to polyester composite materials which are comprised of a polyester polymer and a pre-swelled layered organoclay material.

Specifically, the present invention relates to a composition comprising a
25 polymer having dispersed therein at least one pre-swelled organoclay material comprising

A layered clay material which has been cation exchanged with an organic cation salts represented by Formula I:



35 wherein M represents either nitrogen or phosphorous; X^- represents an anion selected from the group consisting of halogen, hydroxide, or acetate anions, preferably chloride and bromide; R_1 is selected from the group consisting of straight and branched alkyl groups having at least 8 carbon atoms; R_2 , R_3 , and R_4

- 5 are independently selected from straight or branched alkyl groups having 1- to four carbon atoms; and at least one expanding agent which is compatible with said polymer.

Another embodiment of the present invention is a polyester composite comprising at least one polyester having dispersed therein up to about 30 weight
10 percent of an expanded organoclay comprising

- (a) 20 to 80 weight percent of a swellable layered silicate clay such as montmorillonite that has been ion exchanged with an onium salt having one substituent selected from the group consisting of straight and branched alkyl groups having at least 8 carbon atoms and
15 (b) 80 to 20 weight percent of at least one expanding agent.

Although some enhancement of barrier of a polyester occurs by incorporation of an organoclay itself, it was found unexpectedly that a greater improvement in barrier occurred when the organoclay was pre-swelled with an expanding agent.

20 Without being bound by any particular theory, it is believed that the interlayer spacing of the clay increases due to the expanding agent, and as a result, the interaction of the platelet particle layers are weakened to provide improved dispersion in the polyester.

An organoclay is defined here as a swellable layered clay material that has
25 been ion exchanged with an onium ion. An expanding agent is defined here as any material that will increase the basal spacing of an organoclay when introduced into the galleries. An expanded organoclay is defined here as an organoclay that has been pre-swelled with an expanding agent.

These novel polyester composites containing the expanded organoclay
30 exhibit lower oxygen permeability than the polyester or the polyester organoclay blend alone. The improvement in oxygen permeability is clearly apparent in the comparison of film prepared from unmodified poly(ethylene terephthalate) and poly(ethylene terephthalate)-platelet particle composites containing 2 wt % of bis(2-hydroxyethyl) methyl tallow ammonium montmorillonite and (3)
35 poly(ethylene terephthalate)-platelet particle composite containing 2 wt % of bis(2-hydroxyethyl)methyl tallow ammonium montmorillonite and pre-swelled with the

5 expanding agent poly(ethylene oxide) with molecular weight of 3350. The oxygen permeabilities of (1), (2), and (3) are 12, 11, and 6 cc-mil/100 in²-24 hours-atm, respectively. These examples and other examples demonstrating this invention are shown in Table 1.

10 Organoclay materials

 The compositions of the present invention comprise between about 0.01 and about 25 wt%, preferably between 0.5 and 25 wt%, more preferably between 0.5 and 15 wt% and most preferably between 0.5 and 10 wt% of at least one certain expanded organoclay which is derived from organic and inorganic clay materials.

15 The amount of expanded organoclays is determined by measuring the amount of ash of the polyester-platelet compositions when treated in accordance with ASTM D5630-94, which is incorporated herein by reference.

 The platelet particles of the present invention have a thickness of less than about 2 nm and a diameter in the range of about 10 to about 1000 nm. For the

20 purposes of this invention measurements refer only to the platelet particle and not any dispersing aids or pretreatment compounds which might be used. Suitable platelet particles are derived from clay materials which are free flowing powders having a cation exchange capacity between about 0.3 and about 3 meq/g and preferably between about 0.8 and about 1.5 meq/g. Examples of suitable clay

25 materials include mica-type layered phyllosilicates, including clays, smectite clays, sodium montmorillonite, sodium hectorite, bentonites, nontronite, beidellite, volkonskoite, saponite, sauconite, magadiite, vermiculite, mica, kenyaite, synthetic sodium hectorites, and the like. Clays of this nature are available from various companies including Southern Clay Products and Nanocor, Inc. Generally the clay

30 materials are a dense agglomeration of platelet particles which are closely stacked together like cards.

 Preferred swellable layered clay materials are phyllosilicates of the 2:1 type having a cation exchange capacity of 50 to 200 milliequivalents per 100 grams of mineral. The most preferred swellable layered clay materials are smectite clay

35 minerals, specifically montmorillonite.

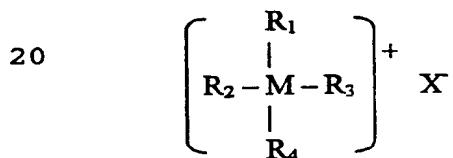
5 Other non-clay materials having the above described ion exchange capacity and size, such as chalcogens may also be used as the source of platelet particles under the present invention. These materials are known in the art and need not be described in detail here.

10 Dispersions of platelet particles having large basal spacing (greater than about 3 nm) have not been previously disclosed. Previous patents and applications have claimed to produce polyesters containing intercalated or exfoliated platelet particles, as indicated by large basal spacings or the lack of a detectable basal spacing by X-ray, however, the results could not be reproduced, particularly in polyesters.

15

Cation Exchange Materials

Useful organic cation salts for the process of this invention can be represented by Formula I:



25 Wherein M represents nitrogen; X^- represents an anion selected from the group consisting of halogen, hydroxide, or acetate anions, preferably chloride and bromide; R_1 is selected from the group consisting of straight and branched alkyl groups having at least 8 carbon atoms; R_2 , R_3 , and R_4 are independently selected from organic and oligomeric ligands or may be hydrogen. Examples of useful
30 organic ligands include, but are not limited to, linear or branched alkyl groups having 1 to 22 carbon atoms, aralkyl groups which are benzyl and substituted benzyl moieties including fused ring moieties having linear chains or branches of 1 to 22 carbon atoms in the alkyl portion of the structure, aryl groups such as phenyl and substituted phenyl including fused ring aromatic substituents, beta, gamma
35 unsaturated groups having six or less carbon atoms, and alkyleneoxide groups having 2 to 6 carbon atoms. Examples of useful oligomeric ligands include, but are not limited to, poly(alkylene oxide), polystyrene, polyacrylate, polycaprolactone, and the like.

5 Preferably R₂, R₃, and R₄ are independently selected from straight or branched alkyl groups having 1 to four carbon atoms. More preferably at least one of R₂, R₃, and R₄ is methyl and preferably all of R₂, R₃, and R₄ are methyl.

Examples of useful onium ions includes alkyl ammonium ions, such as dodecylammonium, octadecyl ammonium, and bis(2-hydroxyethyl)octadecyl
10 methyl ammonium, and the like, and alkyl phosphonium ions, such as octadecyltriphenyl phosphonium.

According to the process of the present invention, the selected cation exchanged clay material is treated with at least one expanding agent to separate the agglomerates of platelet particles to individual platelet particles and small tactoids
15 prior to introducing the platelet particles to the polyester. Separating the platelet particles also improves the polyester/platelet interface. Any treatment that achieves the above goals may be used. Examples of useful treatments include intercalation with water soluble or water insoluble polymers, organic reagents or monomers, silane compounds, metals or organometallics, organic cations to effect cation
20 exchange, and their combinations.

The process for manufacturing the polyester composite material of this invention comprises (1) preparing the organoclay material (2) pre-swelling the organoclay material with an expanding agent and (3) incorporating the expanded organoclay in a polyester.

25 The first step of this invention is the preparation of the organoclay material by the reaction of a swellable layered clay with an onium ion. The organoclay materials of this invention may be prepared by dispersing the clay in hot water, most preferably from 50 to 80° C, adding the onium ion with agitation, then blending for a period of time sufficient for the onium compound to exchange most
30 of the cations, usually sodium ions, associated with the layers of the clay. It is desirable to use a sufficient amount of the onium ions to exchange most of the cations present in the galleries. The organoclay material is isolated by methods known in the art, such as filtration or centrifugation.

The second step of this invention is to pre-swell the organoclay with an
35 expanding agent. Although several methods are available to incorporate the expanding agent within the organoclay, such as melt mixing of the expanding agent

5 and organoclay, spray drying of a mixture of the expanding agent and organoclay, or preparation of the organoclay in the presence of the expanding agent, the most expedient method for this invention was to dissolve or suspend both the expanding agent and organoclay in a solvent, such as methylene chloride, then evaporate off the solvent to provide the expanded organoclay.

10 The expanding agents that are useful for this invention encompass a wide range of polymer compositions from oligomers with low molecular weight to high molecular weight polymers. Preferred polymers are compatible or miscible with the polyester to ensure clarity of the final product.

Suitable expanding agents are poly(ethylene oxide), poly(caprolactone), and
15 polyesters comprising residues from at least one dibasic acid and one glycol. In some cases it may be necessary to use more than one glycol to improve miscibility of the expanding agent in organic solvents. The primary dibasic acids are terephthalic, isophthalic, naphthalenedicarboxylic, 1,4-cyclohexanedicarboxylic acid, sodiosulfoisophthalic acid and the like. Typical glycols used in the polyester
20 include those containing two to about ten carbon atoms. Preferred glycols include ethylene glycol, diethylene glycol, 1,4-butanediol, 1,3-propanedimethanol, and 1,4-cyclohexanedimethanol. Molecular weights of these polymers can range from 250 to 25,000.

The third step of this invention is to incorporate the expanded organoclay
25 material into a melt-processible polyester. This process is directed toward preparation of polyester composites wherein the dispersed phase is preferably comprised of individual layers of the layered clay material or tactoids of less than about ten layers having a basal spacing greater than about 30 angstroms. The intercalated clay mineral component of the compound of this invention is present in
30 amounts up to 30 weight percent, more preferable up to about 15 weight percent. The polyester component of the compound of the present invention is present in amounts of at least about 70 weight percent, more preferably at least 85 weight percent.

One method of incorporation of the expanded organoclay into a polyester is
35 the polycondensation of monomers to the polyester in the presence of the expanded organoclay material. The polyester in the present invention may be produced using

5 well known polycondensation procedures. The polyester composite prepared in this manner may also be treated with solid state polymerization to attain sufficient inherent viscosity to permit melt processing.

Another method of incorporation is by the melt extrusion of a blend of the expanded organoclay and a melt-processible polyester. Conventional polymer and
10 additive blending techniques are used in which the polymer is heated to a temperature sufficient to form a polymer melt and the desired amount of the expanded organoclay is added in a suitable mixer, for example an extruder, a Banbury Mixer, and the like. The process should subject the mixture with sufficient shear to delaminate at least 90% by weight of the intercalated material
15 into individual layers. The polyester composite prepared in this manner may also be treated with solid state polymerization to attain sufficient inherent viscosity to permit melt processing.

In the expansion of organoclays by method 2, it is preferred that the expanding agent be present in an amount sufficient to provide a fully expanded
20 organoclay. Figure 1 shows X-ray diffraction patterns of the organoclay, tallow methyl dihydroxyethylammonium montmorillonite, that has been expanded in methylene chloride with PETG 6763, commercially available from Eastman Chemical Company, as expanding agent to provide expanded organoclays containing 40 and 60 weight percent of clay. Two X-ray reflections are evident,
25 one at about 3.2 nm, corresponding to the fully expanded organoclay, and another at about 2.2 nm, corresponding to the partially expanded organoclay. These examples show that the expanded organoclay must contain less than about 40 weight percent of clay in order to provide a predominately fully expanded organoclay. Examples of expanded organoclays by method 2 are shown in Table 1.

30 In the expansion of organoclays in water by method 3, a fully expanded organoclay is obtained when the clay content is more than 20% but less than 60% by weight of clay (see Figure 2). Examples of expanded organoclays by method 3 are shown in Table 2.

The expanding agents that are useful for this invention encompass a wide
35 range of polymer compositions from oligomers with low molecular weight to high molecular weight polymers. In method 2 described above, preferred polymers are

5 those that are soluble or will suspend readily in organic solvents, such as methylene chloride or toluene. Preferred organoclays are those that can be swelled by these solvents, thus allowing easy access of the expanding agent to the interlayer spacing of the organoclay. Preferred polymers used as expanding agents should be compatible or miscible with the polyester used to form the final article if clarity is
10 needed in the product.

Suitable expanding agents are poly(caprolactone), poly(dimethylsiloxane), polyepoxides, polystyrene, polyacrylates, polycarbonates, polyurethanes, polysulfones, polyethers, polyketones, polyamides, and polyesters comprising residues from at least one dibasic acid and one glycol. In some cases in the
15 preparation of polyesters it may be necessary to use more than one glycol to improve miscibility of the expanding agent in organic solvents. The primary dibasic acids are terephthalic, isophthalic, octadecyloxyisophthalic acid, naphthalenedicarboxylic, 1,4-cyclohexanedicarboxylic acid, sodiosulfisophthalic acid and the like. Typical glycols used in the polyester include those containing
20 two to about ten carbon atoms. Preferred glycols include ethylene glycol, diethylene glycol, 1,4-butanediol, 1,3-propanedimethanol, and 1,4-cyclohexanedimethanol. Molecular weights of these polymers can range from 250 to 25,000. Monomeric species may also act as expanding agents. Among these are Zonyl A and vitamin

25 For convenience in this work, the expanded organoclay was coated on the surface of the polyester pellets prior to extrusion. This was accomplished by blending polyester pellets with the expanded organoclay in methylene chloride followed by evaporation of the methylene chloride.

30 Polymers

The treated organoclay of the present invention may be combined with a wide variety of polymers including thermoplastic polymers and mixtures thereof and vulcanized and thermoplastic resins. Thermoplastic resins include polylactones, polyurethanes, linear long chain diols, polyether diols, polysulfones, polyether
35 ether ketones, polyamides, polyesters, polyesteramides, poly(arylene)oxides, polyarylene sulfides, polyetherimides, vinyl polymers and their copolymers,

5 ethylene acrylic acid copolymers, ethylene vinyl alcohol copolymers, acrylonitrile copolymers, methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers, methacrylated butadiene-styrene copolymers, polyolefins, cellulose ester plastics and the like. Many suitable polymers are disclosed in WO 93/04118, the disclosure of which is incorporated herein by reference. Particularly suitable are polyesters
10 for incorporation of the expanded organoclays which include at least one dibasic acid and at least one glycol. The primary dibasic acids are terephthalic, isophthalic, naphthalenedicarboxylic, 1,4-cyclohexanedicarboxylic acid and the like. The various isomers of naphthalenedicarboxylic acid or mixtures of isomers may be used, but the 1,4-, 1,5-, 2,6-, and 2,7-isomers are preferred. The 1,4-
15 cyclohexanedicarboxylic acid may be in the form of cis, trans, or cis/trans mixtures. In addition to the acid forms, the lower alkyl esters or acid chlorides may be also be used.

The dicarboxylic acid component of the polyester may optionally be modified with up to about 50 mole percent of one or more different dicarboxylic
20 acids. Such additional dicarboxylic acids include dicarboxylic acids having from 6 to about 40 carbon atoms, and more preferably dicarboxylic acids selected from aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of suitable
25 dicarboxylic acids include terephthalic acid, phthalic acid, isophthalic acid, naphthalene- 2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, diglycolic acid, 1,3-phenylenedioxy diacetic acid and the like. Polyesters may be prepared from two or more of the
30 above dicarboxylic acids.

The polymer may also contain small amounts of trifunctional or tetrafunctional comonomers to provide controlled branching in the polymers. Such comonomers include trimellitic anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, trimellitic acid, pyromellitic acid and other polyester
35 forming polyacids or polyols generally known in the art.

5 Typical glycols used in the polyester include aliphatic glycols containing from two to about ten carbon atoms, aromatic glycols containing from about 6 to about 15 carbon atoms and cycloaliphatic glycols containing from about 7 to about 14 carbon atoms. Preferred glycols include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol and the like.

10 Resorcinol and hydroquinone are preferred aromatic glycols. The glycol component may optionally be modified with up to about 50 mole percent of one or more additional diols. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include: diethylene glycol, triethylene glycol, 1,4-

15 cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(2-hydroxyethoxy)-benzene, 1,3-di-(2-

20 hydroxyethoxy)benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane and the like. 1,4-Cyclohexanedimethanol may be used as the cis, trans or cis/trans mixtures. Polyesters may be prepared from one or more of the above diols.

25 Bifunctional compounds such as hydroxybenzoic acid may also be included.

 The amount of expanded organoclay incorporated into the polyester may vary widely depending on the intended use of the composite. The amount of material employed, based on the clay content, is preferably from about 2 to 20 % by weight of the mixture.

30 The polyester containing the homogeneously distributed layered clay can be formed into film by suitable film-forming methods, such as extrusion or pressing, or when the appropriate polyester is used, may be blown into bottles.

 All inherent viscosities are determined at 25° C using 0.5 g of polymer per 100 mL of a solvent consisting of 60 parts by weight phenol and 40 parts by weight tetrachloroethane. The melting temperatures are determined by differential

35 scanning calorimetry (DSC) on the second heating cycle at a scanning rate of 20° C

5 per minute after the sample has been heated to melting and quenched to below the glass transition temperature of the polymer. Oxygen permeability measurements were obtained according to ASTM D-3985 using a MOCON Oxtran-1000 instrument at 30 C and 68% relative humidity with pure oxygen permeant and nitrogen gas carrier. WAXS measurements of the spacings of the <001> plane
10 were performed on powdered samples using a 2 circle Scintag PAD V diffractometer equipped with a Peltier solid state detector using Cu K α radiation from a closed tube operated at 20 ma and 45 kV.

Example 1

15 This example illustrates the method for preparing the organoclay materials used in this invention. Sodium montmorillonite (10 grams, 9.5 milliequivalents, clay supplied by Southern Clay Products and reported to have a cation exchange capacity of 95 milliequivalents/100 grams) was mixed with 490 ml of water at 60 C in a Vitamix blender to form a 2% by weight slurry of clay in water. Bis(2-
20 hydroxyethyl) methyl tallow ammonium chloride (4.0 grams, 9.5 milliequivalents) commercially available as a 74% solution as Ethoquad T/12 was added to the Vitamix blender and the mixture blended at high speed for one minute. The solids formed were removed by filtration on a Buchner funnel. The product was reslurried in 250 ml of water in a Vitamix blender, filtered again, and dried in a
25 circulating air oven at 60 C for 16 hours. The product exhibited a basal spacing by X-ray diffraction of 2.0 nanometers.

Example 2

This example illustrates the method used for preparing the expanded
30 organoclay materials used in this invention from an organic solvent. The expanding agent polydimethylsiloxane, carbinol terminated (Petrach Systems, Inc.) (2.26 grams), was dissolved in 60 ml of methylene chloride. The organoclay bis(2-hydroxyethyl) methyl tallow ammonium montmorillonite (2.73 grams) was then added and the mixture blended at high speed in a Vitamix blender. The solvent
35 was then allowed to evaporate to provide a solid material having a basal spacing by X-ray diffraction of 4.5 nanometers.

5 **Examples 3-16**

The compositions are prepared according to the procedure set forth in Example 2 and are listed in Table 1. The organoclay used is bis(2-hydroxyethyl) methyl tallow ammonium montmorillonite and the weight percent of clay used in each example based on total weight of expanded organoclay is 40 weight percent.

- 10 Ethoquad 18-25 is commercially available from AKZO Chemical Company. PD7610 is commercially available from Anderson Chemical Company. AQ55 and PETG 6763 are commercial available polyesters made by Eastman Chemical Company. Epon 828 is available from Shell Chemical Company. SCX800 is made by S. C. Johnson Wax, Co.

15

Table 1

Example	Expanding Agent	X-Ray Basal, nm
Comparative Example 1	None	2.0
3	Polyethylene glycol distearate	4.2
4	Zonyl A	3.8
5	Polysar 101 polystyrene	3.7
6	Vitamin E	3.6
7	Ethoquad 18-25	3.5
8	Polyglycidylacrylate PD7610	3.4
9	AQ55	3.2
10	PETG 6763	3.1
11	Epon 828	3.1
12	Polycaprolactone	3.0
13	Polymethacrylate SCX800B	3.0
14	Poly(vinyl pyrrolidone)	2.9
15	Makrolon 2608 Polycarbonate	2.9
16	Poly(ethylene oxide) mw 3350	2.4

5 Example 17

 This example illustrates the method used for preparing the expanded organoclay materials from an aqueous medium. . The water soluble polyester AQ 55 (5.0 grams) was dissolved in 250 ml of hot water in a Vitamix blender.. Sodium
10 montmorillonite (5.0 grams, 4.75 milliequivalents, clay supplied by Southern Clay Products and reported to have a cation exchange capacity of 95 milliequivalents/100 grams) was added to the blender and blended for one minute. Octadecyl bis(polyoxyethylene[5]amine (2.32 grams, 4.75 meq), commercially
15 available as Ethomeen 18/15 from AKZO Chemical Company, was suspended in 25 ml of water and 4.88 g of 0.973 N HCl was added to form the ammonium salt which immediately dissolved. This ammonium salt solution was then added to the Vitamix blender containing the AQ 55 and clay and the mixture was blended at high speed for one minute. The solids formed were removed by filtration on a Buchner funnel. The product was reslurried in 250 ml of water in a Vitamix
20 blender, filtered again, and dried in an air circulating oven at 60 C for 16 hours. The product exhibited a basal spacing by X-ray diffraction of 4.1 nanometers.

Examples 18 -25.

25 The compositions are prepared according to the procedure set forth in Example 17 and are listed in Table 2. The expanding agent in each case is AQ 55 and the weight percent of clay used in each example based on total weight of expanded organoclay is 40 weight percent.

5

Table 2

Examples	Onium ion used with sodium montmorillonite	X-Ray Basal, nm Organo-clay	X-Ray Basal, nm Expanded Organo-clay
18	Octadecyl-trimethyl ammonium	2.0	3.9
19	Octadecyl dihydroxyethyl ammonium	1.7	3.8
20	Octadecyl benzyldimethyl ammonium	2.1	3.8
21	Tallow-methyl-dihydroxylethyl ammonium	1.9	3.6
22	Dodecyltrimethyl ammonium	1.6	3.2
23	Hexadecyltributyl phosphonium	2.2	3.1
24	Octadecylammonium	1.7	3.1
25	Dodecylammonium	1.4	3.0
Comparative Example 2	Tridodecylammonium	2.5	2.7
Comparative Example 3	Tetramethyl	1.4	1.4

10 Comparative Example 1

The procedure of Example 2 was repeated except that no expanding agent was used. The basal spacing of the product was 2.0

Comparative Example 2

15 The procedure of Example 17 was repeated except that tridodecylammonium chloride was used. The product had a basal spacing of 2.7 nanometers.

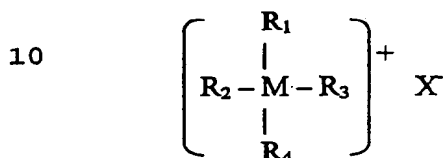
5 **Comparative Example 3**

The procedure of Example 17 was repeated except that tetramethylammonium chloride was used. The product had a basal spacing of 1.4 nanometers.

5

WE CLAIM:

1. A composition comprising alayered clay material which has been cation exchanged with an organic cation salts represented by Formula I:



15 wherein M represents either nitrogen or phosphorous; X^- represents an anion selected from the group consisting of halogen, hydroxide, or acetate anions, preferably chloride and bromide; R_1 is selected from the group consisting of straight and branched alkyl groups having at least 8 carbon atoms; R_2 , R_3 , and R_4 are independently selected from straight or branched alkyl groups having 1 to four
20 carbon atoms; and at least one expanding agent which is compatible with said polymer.

2. The composition of claim 1 wherein R_1 is selected from the group consisting of straight and branched alkyl groups having between 8 and 25 carbon atoms.

25 3. The composition of claim 1 wherein R_1 is selected from the group consisting of straight and branched alkyl groups having between 12 and 20 carbon atoms.

4. The composition of claim 1 wherein R_2 , R_3 , and R_4 are independently selected from straight or branched alkyl groups having 1 to four carbon atoms and
30 at least one of R_2 , R_3 , and R_4 is methyl.

5. The composition of claim 1 wherein R_2 , R_3 , and R_4 are each methyl.

6. The composition of claim 1 wherein said polymer is selected from the group consisting of thermoplastic polymers and mixtures thereof and vulcanized and thermoplastic resins.

35 7. The composition of claim 1 wherein said polymer is at least one thermoplastic resins selected from the group consisting of polylactones, polyurethanes, linear long chain diols, polyether diols, polysulfones, polyether ether ketones, polyamides, polyesters, polyesteramides, poly(arylene)oxides,

5 polyarylene sulfides, polyetherimides, vinyl polymers and their copolymers, ethylene acrylic acid copolymers, ethylene vinyl alcohol copolymers, acrylonitrile copolymers, methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers, methacrylated butadiene-styrene copolymers, polyolefins, cellulose ester plastics.

8. The composition of claim 1, 2, 3 or 4 wherein said polymer is at least
10 one polyester.

9. The composition of claim 8 wherein said polyester is derived from at least one dibasic acid and at least one glycol.

10. The composition of claim 8 wherein said dibasic acid comprises terephthalic, isophthalic, naphthalenedicarboxylic, 1,4-cyclohexanedicarboxylic
15 acid and mixtures thereof.

11. The composition of claim 10 wherein said dibasic acid further comprises up to about 50 mole percent of one or more second dicarboxylic acids selected from the group consisting of aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon
20 atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms.

12. The composition of claim 8 wherein said glycol is selected from the group consisting of aliphatic glycols containing from 2 to about 10 carbon atoms, aromatic glycols containing from about 6 to about 15 carbon atoms and cycloaliphatic glycols containing from about 7 to about 14 carbon atoms.

13. The composition of claim 12 wherein said glycol further comprises up to about 50 mole percent of one or more additional diols selected from the group consisting of cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms.

14. The composition of claim 1 wherein said layered clay material is
30 incorporated in an amount between about 2 to 20 % by weight of the mixture.

15. A composition comprising at least one polymer having dispersed therein at least one layered clay material which has been cation exchanged with an organic cation salt having one substituent R_1 selected from the group consisting of straight and branched alkyl groups having at least 8 carbon atoms; and at least one
35 expanding agent which is compatible with said polymer, wherein basal spacing between the layers of the layered clay material is greater than about 3.4.

- 5 16. A composition comprising at least one polyester having dispersed
therein at least one layered clay material which has been cation exchanged with an
organic cation salt having one substituent R_1 selected from the group consisting of
straight and branched alkyl groups having at least 8 carbon atoms; and at least one
expanding agent which is compatible with said polymer, wherein basal spacing
10 between the layers of the layered clay material is greater than about 3.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 97/24103

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B33/44 C08K9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 30950 A (DOW CHEMICAL CO ; SOUTHERN CLAY PROD INC (US)) 28 August 1997 see claims 1,2 ---	1-16
X	EP 0 459 472 A (TOYODA CHUO KENKYUSHO KK) 4 December 1991 see page 3, line 19 - line 34 see claims 1-4 ---	1-16
A	MASAYA KAWASUMI: "Preparation and mechanical properties of polypropylene-clay hybrids" MACROMOLECULES, vol. 30, 1997, pages 6333-6338, XP002077293 cited in the application -----	1-16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- "&" document member of the same patent family

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Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Siemens, T

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/24103

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